

PATENT SPECIFICATION

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(54) ELECTRICAL IGNITER ELEMENTS

(71) We, THE CARBORUNDUM COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 1625 Buffalo Avenue, Niagara Falls, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to igniter elements, and more particularly to igniter elements suitable for use at high temperature duty which requires rapid heating, and/or low power consumption, such as is required for igniters for gaseous fuels.

An igniter element which has suitable electrical resistivity and high stability at high temperatures and in corrosive environments has many potential electrical and thermal applications. An application of particular interest for such a material is as an igniter for combustible gases. An important behavioural property for such an application is the relationship between electrical resistivity and temperature, referred to as the temperature-resistance characteristic. Particularly desirable for preventing electrical short circuits (caused by failure of the element) is a temperature-resistance characteristic which is flat or rising at higher temperatures.

The need for a low power consumption electrical ignition means to replace pilot lights in gas ranges and ovens has become imperative in view of safety factors and limited fuel availability. It has been found that constantly burning pilot lights can account for a considerable amount of energy consumed by a gas stove. Pilot lights also produce considerable amounts of nitrogen oxides, a chief component of smog. In the closed environment of the home, emissions from these ever-burning flames can possibly exceed the established safe nitrogen oxide limits.

In the field of fuel burning or combustion systems, it has been previously known to employ refined silicon carbide igniters because of

their ability to withstand exceedingly high operating temperatures without disintegration or material deterioration. Furthermore, they are non-corrosive and substantially inert to the destructive effects of fuel combustion products. However, such silicon carbide igniters have been prepared from self-bonded silicon carbide, such as the spiral igniter thermistor assembly set forth by U.K. Patent 1,144,540 and the igniter set forth by U.K. Patent 1,104,054. Such igniters have been less than fully satisfactory for all conditions of operation, however, due to fragility, high cost, voltage requirements, and power consumption.

The purpose of the present invention is to overcome the disadvantages of the prior art by providing an igniter element which is more dependable, readily reproducible, physically strong, capable of achieving high temperatures rapidly and repeatedly, and which may operate at lower power consumption and lower voltages than prior art devices.

It is thus an object of this invention to provide igniter elements, capable of achieving gas ignition temperatures, which operate at relatively low power consumption, and are suitable for a variety of voltages, such as from 6 to 220 volts.

According to the present invention there is provided a method of producing an igniter element comprising the steps of:

- a) forming a shaped body consisting essentially of flexible discontinuous laminar graphite;
- b) covering the body with at least 4 times the weight of said laminar graphite of a siliconising mix comprising 65 to 91% by weight of silicon in the form of elemental silicon or a compound capable of yielding elemental silicon on heating, 4 to 25% of graphitic carbon and 1 to 15% of a carbonaceous binder;
- c) heating the body and mix at a temperature of at least 1450°C and, if the mix contains a silicon yielding compound, at least to the temperature at which said compound yields silicon, said heating being conducted for a sufficient time to convert substantially all

of the graphite of said body to silicon carbide; and

- 5 d) further heating the obtained silicon carbide body to a temperature of higher than that used in step (c) and in the range of 1800 to 2500°C.

Preferably step (c) is conducted at a temperature of 1450 to 2200°C.

- 10 The invention will now be described by way of example only, with reference to the drawings.

Fig. 1 represents a frontal view of one igniter element produced in accordance with the present invention;

- 15 Fig. 2 represents a frontal section of an igniter element produced in accordance with the present invention;

Fig. 2a represents a side elevation of the element of Fig. 2, and

- 20 Fig. 3 represents a graphical representation of the temperature-resistance characteristics of various igniter elements.

- 25 Silicon carbide has long been known as a high temperature refractory material, and has also been used for high temperature electrical heating elements. In accordance with the present invention, an igniter element is produced by the siliconization of a discontinuous laminar graphite structure. Said siliconization is not meant to encompass merely the formation of a silicon carbide surface layer upon the substrate, but the total conversion of the entire graphite substrate to silicon carbide of controlled properties. The igniter element
- 30 thus provided has the advantages of a very rapid response, great versatility, and simplicity of preparation.

- 35 The siliconization of carbon substrates has been known in the prior art, e.g. from U.K. Patent 583,039. In that instance, however, silicon carbide is formed *in situ* by subjecting a carbon body having a continuous skeletal structure to the action of elemental silicon at a temperature well above the melting point of silicon. The silicon carbide formed thus retains a skeletal and reticular structure.

- 40 Graphites are known to be made up of layer planes of hexagonal arrays or networks of carbon atoms. These layer planes of hexagonally arranged carbon atoms are substantially flat and are oriented or ordered so as to be substantially parallel and equidistant of one another. Graphites thus may be characterized as laminated structures of carbon, that is structures consisting of superposed layers of laminae of carbon atoms joined together. The present invention utilizes, as a starting material, a sheet material consisting essentially of graphite, which is preferably free of any binding or bonding material. Such a flexible, binderless graphite sheet material may be produced by compressing or compacting, under a predetermined load and in the absence of a binder, expanded graphite particles so as to
- 45 form a substantially flat, flexible, integrated

graphite sheet. It is noted that the expanded graphite particles utilized maintain the compression set once compressed. The density and thickness of the sheet material may be varied by controlling the degree of compression. Suitably, the density of the sheet material may be within the range of from about 40 to about 100 lbs./cu. ft., and preferably from 10 to 80 lbs./cu. ft. Such sheet material may be provided with a uniform thickness in the range of from 0.0001 inch (0.1 mil) to about 0.500 inch (500 mil.). Ribbons of this sheet material may readily be cut to give a body of the desired size and configuration for use in the method of the invention. (The term "ribbon", as used herein, shall be understood to refer to a flat, narrow strip of sheet material, having a thickness of 0.500 inch or less, and preferably less than 0.050 inch.) Igniter elements may be prepared by the siliconization of such shaped ribbons in accordance with the following disclosure. It has been found, however, that a thickness of less than 0.100 inch, and preferably less than 0.050 inch, is most suitable for siliconization. It is to be noted that an interrelationship between thickness, density and siliconization capability is believed to exist, in that case of siliconization decreases with increasing thickness and density. Thus, if thickness of the ribbon is increased, the density may be decreased to compensate. It is further noted that an expansion in thickness, amounting to 60 to 70 percent occurs upon siliconization of such sheet materials.

The flexible graphite sheet material produced in the above manner may be modified in many ways. For example, in the formation thereof, impregnants or additives, such as dopants, may be incorporated or mixed with the expanded graphite and the composition compressed to for the desired sheet material. Likewise, one or both sides or surfaces of the soft flexible graphite sheet material may be embossed, quilted or otherwise provided with a pattern. The flexible graphite material thus produced may be formed by wrapping, rolling, or otherwise working, to provide solid and hollow articles or products of any configuration desired. Thin sheets, such as from 0.005 to 0.015 inch may be laminated together to form a thicker sheet material. However, it has been found that delamination frequently occurs when laminated sheets of greater than 0.050 inch are subjected to siliconization.

It has been found that graphites having a high degree of orientation may be treated so that the spacing between the superposed carbon layers or laminae can be appreciably opened so as to provide a marked expansion in the direction perpendicular to the layers, in accordance with the teachings of U.S. Patent 3,404,061 issued October 1, 1968. Thus, an expanded or intumesced graphite structure may be formed, in which the laminar character is substantially retained. By expand-

ing particulate graphite so as to have a final thickness which is at least 80 or more times the original thickness, a graphite material is formed which may be formed, without the use of a binder or bonding agent, into cohesive or integrated sheets, e.g., webs, papers, strips, tapes or the like. Additionally, the flexible graphite sheet material thus formed can be cut or slit into narrow strips which can be used to form woven or braided graphite fabric or cloth, or suitably rolled or wound or otherwise worked to form solid or hollow structures.

Upon drying and finishing of such a flexible graphite sheet, said material may be cut to a body of the desired configuration of the final igniter element to be produced. It is possible, as previously indicated, to produce configurations of almost any desired shape or dimension.

The graphite starting material is then covered with a siliconizing mix. This operation may be performed in a graphite crucible or other suitable container. The amount of siliconizing mix used is preferably 20 times the green weight of the body being fashioned, with a minimum of 4 times the green weight of the body. The siliconizing mix comprises a silicon source (either elemental silicon or a compound capable of yielding elemental silicon), in a concentration such that the mix comprises from 65 to 91 percent by weight of silicon (in elemental or combined form), from 4 to 25 percent graphitic carbon, and from 1 to 15 percent of a carbonaceous resinous binder material. It is essential that the siliconizing mix contains sufficient silicon to convert all of the carbon present to silicon carbide. Suitable sources of silicon include silicon metal, silica, and silicon nitride. It is necessary to have free graphitic carbon present in the siliconizing mix in order to form a loose silicon carbide skeleton coating upon the silicon carbide body formed, to thereby inhibit binding of the body to the siliconizing mix, thus yielding a homogeneous body, having a minimum of excess silicon incorporated therein. The proportions of silicon and carbon are so selected as to provide a stoichiometric relationship when taking into account the amount of carbon present in the graphite material being siliconized. Dopants may be included in the siliconizing mix in small proportion, or provided otherwise as hereinafter described.

The laminar graphite body and siliconizing mix are then heated to a siliconizing temperature. If conducted in a vacuum, it has been found that a temperature of from 1450°C to 1850°C, for up to 60 minutes, is sufficient. When using a tube furnace at atmospheric pressure in an inert or doping atmosphere, a temperature of from 1800° to 2200°C is appropriate. The minimum temperature necessary in either instance is, if a silicon yielding compound is used as the source

of silicon, a temperature in excess of that at which free silicon is produced in the mix.

The graphite body and siliconizing mix are heated for sufficient time to convert essentially all carbon present to silicon carbide. Thereupon, the body and mix may be allowed to cool to room temperature and the body cleaned, i.e. by removal of excess siliconizing mix.

Modifications of the properties of the thus obtained body may be achieved by the refiring or reheating step. For example, refired units are capable of being heated to much higher temperatures. Refiring may be accomplished by heating the silicon carbide body to a temperature in excess of the siliconizing temperature previously used. For example, refiring may be accomplished by heating to from 1800° to 2200°C in vacuum, or from 2000° to 2500°C in an inert or doping atmosphere. It is to be recognized, of course, that the refiring may merely constitute an additional heating beyond the original siliconization heating, without an intermediary cooling. Thus, the heating may comprise a step-wise or staged elevation to a siliconizing temperature followed by an increase in temperature to a refiring temperature. Refiring results in the removal of excess silicon from the silicon carbide body, and is also believed to cause grain growth and phase changes in the silicon carbide.

As previously indicated, it is possible to accomplish doping of the silicon carbide body by incorporating dopant during siliconization, either in the siliconizing mix or in the atmosphere employed. Alternatively, dopants may be provided during refiring, such as by refiring in a nitrogen atmosphere. After refiring, the igniter element thus formed is allowed to cool to room temperature, and is cleaned to remove any excess silicon or other material thereupon. The element thus formed may then be provided with electrical contacts in any suitable manner, such as by coating of any suitable electrical conducting material, e.g. aluminium. Such a coating is deposited on the exterior surfaces of the connecting portions of the silicon carbide element adjacent the end portions thereof, in order to provide electrical terminals. The metal chosen should have such characteristics, in addition to electrical conductivity, so as to be compatible with the silicon carbide material. The coating may be sprayed on to the igniter element, or it may be applied in any other conventional manner. Suitable materials include the deposition of carbonyl nickel, tungsten, aluminum, gold, silver, etc. Suitable techniques include sputtering, molten bath coating, deposition from the slurry, painting, and vapor deposition. A preferred contact material is tungsten which may be advantageously deposited by sputtering.

Doping of the silicon carbide coating is re-

quired to achieve specific resistivities as desired. The dopant utilized may be either of the n-type or p-type. The effects of refiring and doping are illustrated in Fig. 3, which graphically demonstrates the relationship between exemplary resistance and temperature for different silicon carbide elements. Thus, it may be seen that a positive temperature-resistance relationship may be achieved by the use of the proper dopant and/or processing conditions. It is to be noted that essentially pure silicon carbide elements have resistances of about 10^6 ohm-cm or higher. Thus the presence of a dopant such as phosphorus, nitrogen, boron, or aluminum, is desirable to lower the resistance of the body to a useful level. Other suitable dopants may, of course, be used.

For the dopant, suitable compounds may be employed during refiring or suitable dopants may be provided either in the siliconizing cover mix or the siliconization atmosphere. For example, nitrogen may be provided as a gas or as the decomposition product of acetonitrile. Solid sources include elemental or compound forms of aluminum, boron, and phosphorus. Such substances may be incorporated in the silicon carbide in a concentration of from 10 percent to 10^{-3} percent by weight.

Mixtures of dopants may be used to achieve specific goals. For example, a mixed dopant comprising boron and nitrogen may be utilized to achieve a temperature-resistivity which is negative at temperatures below about 1000°C and positive above that point. Localized doping may also be utilized to achieve preferential areas of low resistivity.

A typical igniter element may be made as demonstrated in the drawings, Figs. 1 and 2, which are illustrative of configurations which are considered suitable for elements, such as prepared in accordance with the present invention. In Fig. 1, the body, 1, has a relatively narrow high temperature zone 2, and broader base or contact area 3 formed by the legs thereof. The thickness of such a body may suitably be on the order of about 0.010 inch. This particular configuration demonstrates a suitable combination of surface areas such as to keep the legs of the body relatively cool while maintaining sufficient resistance to limit amperage to the hot zone 2. Figs. 2 and 2a represent an alternative form of igniter element wherein the silicon carbide foil element 1, is in a configuration which may be referred to as a hairpin configuration, with the legs 3 supported by electrical contact media 4, prepared from an electrically conductive base material such as graphite or silicon carbide. An appropriate potting cement may be used to attach the silicon carbide foil to the base. The hot zone of the element of Figs. 2 and 2a is in the restricted or constricted zone designated as 2. It is desirable to limit the hot

zone or tip area in order to require a minimum amount of power. This may be accomplished by reducing the surface area of silicon carbide in the hot zone or tipped area relative to the cool zone or leg. With proper design, an igniter element will have the desired low power consumption, the desired temperature at the hot zone, and relatively cool contact points. The constricted or narrowed portion of the elements demonstrated functions as the tip or hot zone, since such zones must carry the same electrical load as the leg or cool portion of the element.

Fig. 3 graphically represents the temperature resistance relationship of two silicon carbide elements. Curve 1 represents a doped element subjected only to siliconization, while curve 2 represents an element subjected to both siliconization and refiring, in a nitrogen atmosphere, at 2400°C . The differing electrical characteristics obtainable are believed to be clearly demonstrated by this figure.

The invention may be further illustrated by the following examples.

Example 1.

A sheet of essentially pure flexible binderless graphite such as described hereinabove, commercially available from the Union Carbide Company under the trade name GRAFOIL (Registered Trade Mark), was cut to the desired configuration prior to siliconization. The piece was shaped as illustrated in Fig. 2, having a restricted or narrow central portion. The dimensions of the piece were $\frac{1}{4}$ inch width in the leg portion, $\frac{1}{8}$ inch width in the restricted or hot zone portion, and length of 2 inches. The thickness of the ribbon was 0.015 inches. A siliconizing cover mix was prepared having the following composition:

Silicon	77 wt. %
Graphite	12 wt. %
Corn Syrup	11 wt. %
Aluminum	<1 wt. %

The corn syrup, used as a binder, is commercially available as KARO (Registered Trade Mark) syrup. The workpiece was covered with the siliconizing mix. The workpiece was subjected to a temperature of 2000°C for about 14 or 15 minutes in an argon atmosphere in a tube furnace, cooled, and refired at 2300°C in argon for 15 minutes. Electrical contacts were provided by alligator clips. The electrical characteristics of the overall unit were found to be suitable for use as an igniter device. An initial voltage of 38.3 went to 29.9 at a temperature of 1070°C , and an amperage of 4.8 amps. Time to ignition was 29 seconds.

Example 2.

A number of igniter elements were prepared in the configuration set forth by Fig. 1 utiliz-

ing a ribbon of discontinuous laminar binderless graphite having a thickness of 0.015 inches. Electrical contacts were applied in each case by either flame spraying aluminum and nickel or by an exothermic flame spray of a mixture comprising 80 percent nickel, 14 percent chromium, and 6 percent aluminum. Varying operating differences and the effect of varying the dopant are set forth in Table 1.

Example 3.

A resistance element in the configuration shown by Fig. 1 was prepared in accordance

with the method of Example 1. Following the refining in argon of 2300°C, the element was again refined, this time at 2400°C in a nitrogen atmosphere for an additional 15 minutes. Alligator clips were applied to the base portions of the element to provide electrical potential. The element evidenced the following properties: at 1000°C, and 23.8 volts, current was 1.42 amps; at 1200°C, and 32.3 volts, a current of 1.53 amps was measured. Thus, the power consumption of the element was found to be 33.8 watts at 1000°C, and 49.4 watts at 1200°C.

TABLE I

Element	Siliconizing Conditions	Refiring Conditions	Room Temperature Resistance (Ohms)
A	Tube furnace, argon atmosphere	Tube furnace, nitrogen atmosphere	4
B	Tube furnace, nitrogen atmosphere	Tube furnace, nitrogen atmosphere	0.4
C	Vacuum, no dopant	Vacuum	230
D	Tube furnace, argon atmosphere	Tube furnace, argon atmosphere	130

WHAT WE CLAIM IS:—

1. A method of producing an igniter element comprising the steps of:

a) forming a shaped body consisting essentially of flexible discontinuous laminar graphite;

b) covering the body with at least 4 times the weight of said laminar graphite of a siliconizing mix comprising 65 to 91% by weight of silicon in the form of elemental silicon or a compound capable of yielding elemental silicon on heating, 4 to 25% of graphitic carbon and 1 to 15% of a carbonaceous binder;

c) heating the body and mix at a temperature of at least 1450°C and, if the mix contains a silicon yielding compound, at least to the temperature at which said compound yields silicon, said heating being conducted for a sufficient time to convert substantially all of the graphite of said body to silicon carbide; and

d) further heating the obtained silicon carbide body to a temperature higher than that used in step (c) and in the range of 1800 to 2500°C.

2. Method as claimed in claim 1 wherein the heating temperature used in step (c) is in the range of 1450 to 2200°C.

3. Method as claimed in claim 1 or 2 where-

in the amount of siliconizing mix used is 20 times the weight of said laminar graphite.

4. Method as claimed in any one of claims 1 to 3, wherein the heating of step (c) takes place in an inert atmosphere.

5. Method as claimed in any one of claims 1 to 3, wherein the heating of step (c) takes place in a vacuum.

6. A method as claimed in any one of claims 1 to 5, wherein the body is doped during step (c).

7. A method as claimed in any one of claims 1 to 5 wherein the body is doped during step (d).

8. A method as claimed in claim 7 wherein doping is achieved by effecting said further heating in an atmosphere containing nitrogen.

9. A method as claimed in any one of claims 1 to 6, wherein step (d) is carried out in an inert atmosphere.

10. A method as claimed in any one of claims 1 to 6, wherein step (d) is carried out in a vacuum.

11. A method of preparing an igniter element substantially as hereinbefore described in any one of the Examples.

12. An igniter element when prepared by the method of any one of claims 1 to 11.

MARKS & CLERK,
7th Floor,
Scottish Life House,
Bridge Street,
Manchester, M3 3DP.
Agents for the Applicants.

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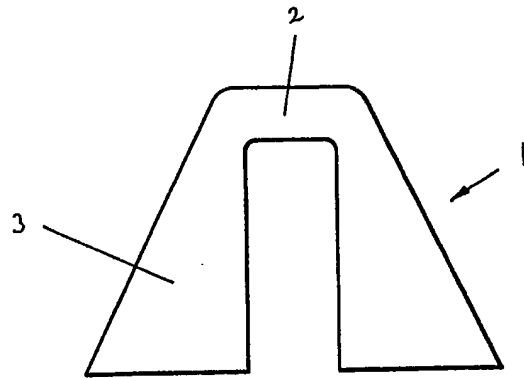


FIG. 1

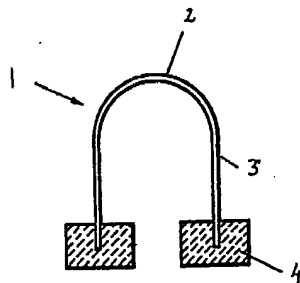


FIG. 2

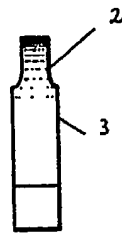


FIG. 2A

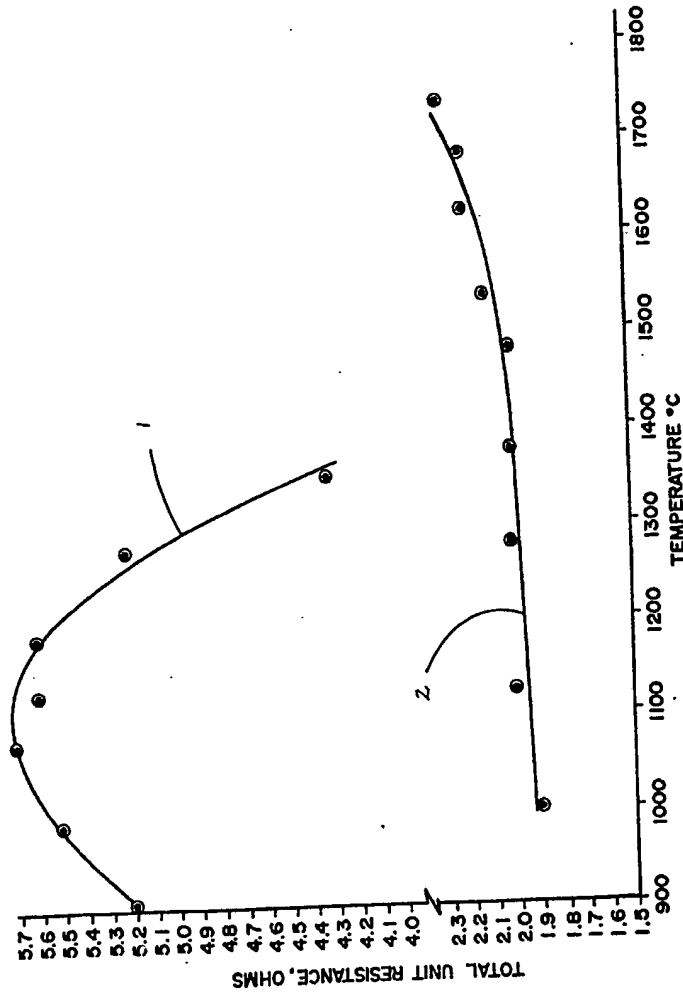


FIG. 3